

# Mechanism of Diamond Nucleation on Titanium Substrate under Very Low Pressure

Qijin Chen

*The state Key Lab of Surface Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China*

*Department of Physics, The University of Chicago, 5720 S. Ellis Ave., Chicago, IL 60637\**

(*\*The corresponding address. Electronic mail: qchen@rainbow.uchicago.edu*)

Zhangda Lin

*The state Key Lab of Surface Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China*

(February 1, 2008)

Nucleation and its mechanism of diamond on titanium substrates under very low pressure was studied using hot-filament chemical vapor deposition. Very high nucleation rates and densities ( $10^8$ - $10^{10}$  cm $^{-2}$ ) were obtained under 1 torr, which were 1-3 orders of magnitude higher than the counterpart (10 $^7$  cm $^{-2}$ ) under conventionally low pressure (tens of torr). The effects of substrate temperature and methane concentration under very low pressure were also investigated, revealing that, overly high substrate temperature leads to a relatively low nucleation density, and that higher CH $_4$  concentration gives rise to a higher density and a higher rate. The nucleation mechanism is discussed in detail. While a large amount of atomic hydrogen creates nucleating sites, sufficient supersaturation of carbon and/or hydrocarbon species on/near the substrate surface is the key factor for nucleation, in competition against the rapid formation of carbide. Very low pressure leads to long mean free path and other benefiting effects, and hence, is critical for rapid, high-density nucleation. Effects of substrate temperature and CH $_4$  concentration are also important. This further implies that C $_2$ H $_x$  (x < 6) and CH $_4$  also contribute to nucleation, but CH $_{1-3}$  dominates under very low pressure. The very-low-pressure method seems to be the only candidate to make diamond deposition on titanium films applicable. It also sheds light on how to increase the diamond growth rate.

81.15.Gh, 81.15.-Z, 81.10.-h, 81.10.Aj

## I. INTRODUCTION

Great progress has been made in recent years in the field of chemical vapor deposition (CVD) of diamond under low pressure. As one of the most important issues, nucleation has always been one of the main focuses of research, as it is the first and also the critical step for diamond synthesis. Technically, to achieve rapid, high-density nucleation is very important for achieving uniform, high-quality diamond films. It is also critical in the effort to achieve hetero-epitaxial diamond films. Theoretically, the mechanism has to be clear to optimize the deposition parameters, to guide the experiments and industrial production process. Both aspects are important for the purpose of fully utilizing diamond, which has so many extraordinary properties.<sup>1</sup> For the most commonly used silicon substrate, high-density nucleation is no longer a problem in either microwave-plasma CVD (MPCVD) or hot filament CVD (HFCVD) up to date. In MPCVD, it was first solved using negative bias method by Jeng *et al*<sup>2</sup> and later developed by Yugo *et al*.<sup>3</sup> The highest density achieved using this method is 10 $^{10}$ -10 $^{11}$  cm $^{-2}$ , reported by Stoner *et al*.<sup>4</sup> Recently, Wolter *et al* applied an ac bias to the substrate and also obtained high-density nucleation.<sup>5</sup> In HFCVD, high-density nucleation on Si has been achieved by Zhu *et al* using negative bias<sup>6</sup> and by Chen and Lin using electron emission.<sup>7,8</sup> An electron-emission-enhancement (EEE) mechanism emerged.<sup>7,8</sup> In

addition to the EEE method, this problem has also been solved using a very-low-pressure technique.<sup>9,10</sup> A density comparable to the highest value achieved in MPCVD was reported on unscratched, mirror-polished Si substrates, with a very rapid nucleation rate and a high uniformity.<sup>10</sup> Apart from these technical developments, the mechanism of diamond nucleation is still not very clear, although models have been postulated to accommodate those specific techniques.<sup>3,4,10,11</sup>

Titanium, in addition to Si, is another important substrate material in diamond synthesis due to its special industrial applications; it has been one of the major materials for the speaker's vibrational membranes. The super-high Young's modulus ( $1.05 \times 10^{12}$  N/m $^2$ ) and the great acoustic velocity (18.5 km/s) of diamond make it alluring to further coat thin Ti films with thin diamond films to achieve high-fidelity acoustics. Unfortunately, Ti as a substrate has not received as much attention as Si. In result, diamond deposition on Ti, especially on thin Ti films, has not been intensively studied.

Two problems make it difficult to deposit diamond films on Ti. First, the Ti substrate undergoes serious hydrogenation and embrittlement in the presence of hydrogen at high temperature during the deposition process. At high temperature, titanium absorbs a great amount of hydrogen to form titanium hydride.<sup>12,13</sup> This problem is usually overlooked when thick Ti substrates are used (0.5 mm or thicker). However, for very thin Ti

substrates, e.g., tens of microns for a typical speaker's membrane, this becomes a predominant problem. Hydrogenation can render the thin Ti wafers very fragile and unusable. The other serious problem lies in the difficulty of getting rapid, high-density nucleation because of the easy formation of very thick intermediate TiC layers (We use TiC to denote various forms of titanium carbide in this paper).<sup>14</sup> This worsens the hydrogenation problem by prolonging the deposition duration. Park and Lee<sup>14</sup> reported that nucleation began only after the TiC layers grew to as thick as 50  $\mu\text{m}$ , and that diamond films became continuous only after  $> 240$  min deposition at the substrate temperature of 700°C. Such a long time at this temperature usually causes very serious hydrogenation for thin Ti substrates.

The (dc and/or ac) bias methods do not seem to be able to solve the problems, as they usually need 30-60 min or even longer for *in situ* pretreatment and nucleation under temperature 650-900°C,<sup>4,11,15</sup> which could cause very serious hydrogenation of the Ti substrates and formation of thick TiC layers. The EEE method seems to be able to get high-density nucleation within a short time. However, using this method, as well as using the bias methods, nucleation proceeds from the edge to the center of the sample,<sup>8,6,16</sup> which may take a pretty long time to get uniform nucleation across a large substrate, and thus, result in the serious problems. All these nucleation enhancing methods seem to fail or need to be modified to adapt to the Ti substrates.

Recently, Chen and Lin<sup>17</sup> reported a two-step procedure to deposit diamond films on thin Ti wafers ( $\sim 40 \mu\text{m}$  thick) with little hydrogenation and little TiC formation. The very-low-pressure technique was employed to get rapid, high-density nucleation ( $10^9 \text{ cm}^{-2}$ ) within 5 min. Thus the nucleation process was dramatically shortened. Oxygen was used to lower the subsequent growth temperature to greatly reduce the hydrogenating speed. So far, the very-low-pressure method seems to be the only practical one for diamond nucleation on thin Ti wafers. In order to fully utilize this technique, optimize the experimental parameters and make clear the mechanism, it is necessary to make clear the detailed process of the nucleation and how it is influenced by other experimental conditions.

Following our previous work, we report in this paper detailed study of the process of diamond nucleation on Ti substrates with increasing nucleation time under very low pressure (1 torr), and the influence of substrate temperature and CH<sub>4</sub> concentration under such pressure. Rapid, high-density nucleation on Ti was achieved within 2 min at a density of  $10^8\text{-}10^{10} \text{ cm}^2$ . While overly high substrate temperature led to a lower density, higher CH<sub>4</sub> concentration increased the nucleation rate and density. The mechanism of diamond nucleation was discussed in detail, revealing the critical prerequisite of high supersaturation of carbon/hydrocarbon on the substrate surface for diamond nucleation. While the pressure effect, which leads to a much higher concentration of reactive

hydrocarbon radicals near the substrate surface, is critical, the temperature and the CH<sub>4</sub> concentration are also important factors, implying that C<sub>2</sub>H<sub>x</sub> ( $x < 6$ ) and CH<sub>4</sub> (through decomposition into CH<sub>3</sub>) also contribute to nucleation, but CH<sub>x</sub> ( $x < 4$ ) is the main hydrocarbon precursor for nucleation under very low pressure.

## II. EXPERIMENTS

Our experiments were conducted in a typical HFCVD device, as reported in ref. 17. To repeat briefly, a  $\phi 140$  mm and 500 mm long fused silica tube was used as a deposition chamber. Tungsten wires of  $\phi 0.2$  mm wound into coils of  $\phi 2.5$  mm were used as filaments, whose temperature was measured by an optical pyrometer. The substrates were polycrystalline Ti wafers in the size of  $0.5 \times 8 \times 10 \text{ mm}^3$ , whose temperature was measured with a thermocouple. The filament-substrate distance was fixed at  $\sim 8$  mm. Before loaded into the deposition chamber, all substrates were scratched with 1.0  $\mu\text{m}$  diamond powder, and then chemically cleaned with acetone in an ultrasonic bath for 10 min. The nucleation conditions were listed in Table I. Please note that the pressure used, 1.0 torr, was much lower than the usual pressure, tens of torr. Subsequent growth was also allowed when necessary. The growth condition will be mentioned where appropriate. Four groups of experiments were done to investigate the detailed process of nucleation with increasing nucleation time and the effects of very low pressure, substrate temperature and CH<sub>4</sub> concentration. The as-deposited samples were characterized mainly with scanning electron microscopy (SEM), while Raman spectroscopy was also used with necessary. The nucleation density was measured from the SEM photos, and the size of the nuclei was measured from the scanned high-resolution image files of the SEM photos with a much higher magnification in Adobe Photoshop on computer.

## III. RESULTS

Fig. 1 shows the SEM surface morphology of the Ti substrates in experiment Group I after (a) 2 min, (b) 3 min nucleation under very low pressure (1 torr) and (c) 3 min nucleation under 1 torr plus 10 min growth under normally low pressure (20 torr). The substrate temperature and CH<sub>4</sub> concentration for nucleation were  $\sim 810^\circ\text{C}$  and 3 vol. %, respectively. The growth conditions were:  $T_f = 2000^\circ\text{C}$ ,  $T_s = 780^\circ\text{C}$ , [CH<sub>4</sub>] = 1.5 vol. %, and  $F = 100$  sccm. The densities in Fig. 1(a) and Fig. 1(b) were measured to be  $1.5 \times 10^{10} \text{ cm}^{-2}$  and  $3 \times 10^9 \text{ cm}^{-2}$ , respectively. Evidently, very high densities were achieved under very low pressure (1 torr) within only 2 min, which was an amazingly high nucleation rate, in contrast to the report by Park and Lee<sup>14</sup> and even that on a Si substrate

under normal pressure. Usually, the nucleation density on a scratched Ti substrate is no larger than that on a scratched Si substrate under usual pressure, which is  $10^7$ - $10^8 \text{ cm}^{-2}$ . Our result was 2-3 orders of magnitude higher, mainly due to the very low pressure. Subsequent growth for 10 min gave rise to a very good crystallinity of the diamond crystallites with an average size of  $0.3 \mu\text{m}$ , as shown in Fig. 1(c). Raman spectrum analysis also confirmed a good quality of the crystallites. The density of the crystallites was approximately the same as that in Fig. 1(b), demonstrating that all the nuclei in Fig. 1(b) were able to grow into a diamond crystallite. In addition, the nuclei distributed very uniformly. An SEM image of the same sample as in Fig. 1(a) with a lower magnification is shown in Fig. 1(d). Scratch marks of the diamond powder are visible. In contrast with the situation for nucleation under normal pressure, however, no preferential nucleation along the marks can be seen. The rough surface of the substrate was believed to be a result of the formation of TiC layer, which was usually very loose and porous, and on top of which nucleation occurred. As the nucleation durations were very short, the TiC layer could not be thick. It should be mentioned that the substrate temperature could not be exactly the same as the processes were so short. Moreover, the scratching for different substrates could not be identical. These might explain the difference between the densities in Fig. 1(a) and (b).

More detailed study of the nucleation process was performed at a higher substrate temperature. Fig. 2 shows the SEM images of the samples in Group II after (a) 0.5 min, (b) 1 min, (c) 2.5 min, (d) 5 min nucleation, (e) 5 min nucleation plus 10 min growth, and (f) 0.5 min nucleation plus 14 min growth. The nucleation conditions are listed in Table I. The difference between Group II and Group I was the temperature. The growth conditions were:  $F = 100 \text{ sccm}$ ,  $p = 20 \text{ torr}$ ,  $[\text{CH}_4] = 1.5 \text{ vol. \%}$ ,  $T_f = 2000^\circ\text{C}$ , and  $T_s = 800^\circ\text{C}$ . A continuous development of the nucleation with time is presented. From Fig. 2(a), 0.5 min seemed to be too short to make the nuclei large enough to be visible, if they formed. After 1 min (Fig. 2(b)), the nuclei became visible under the specific magnification of the SEM photo, although they were still very tiny. The average size of the visible ones was approximately  $0.1 \mu\text{m}$ . The density was approximately  $6 \times 10^7 \text{ cm}^{-2}$ . After 2.5 min (Fig. 2(c)), the nucleation density increased to approximately  $3 \times 10^8 \text{ cm}^{-2}$  and the nuclei became larger, their size being  $\sim 0.15 \mu\text{m}$ . After 5 min, the density was  $\sim 4 \times 10^8 \text{ cm}^{-2}$ , nearly the same as in Fig. 2(c) except that the nucleus size increased to  $\sim 0.3 \mu\text{m}$  and some of them merged. Obviously, the density actually attained to its final value after 2.5 min under the specific experimental conditions. When 10 min growth was allowed following 5 min nucleation, the density of the diamond particles remained the same, while the size grew to  $\sim 0.4 \mu\text{m}$ , as shown in Fig. 2(e). From 2.5 min (Fig. 2(c)) to 5 min (Fig. 2(d)), the size grew approximately linearly with the nucleation time. Fig. 2(e) indicates that

the deposition rate under normal pressure (20 torr) was much lower than that under very low pressure (1 torr). Fig. 2(f) was used to determine whether or not nuclei formed within the first 0.5 min; 14 min growth was allowed after 0.5 min nucleation. The particle density was  $\sim 4 \times 10^8 \text{ cm}^{-2}$ , and the particle size averaged  $0.2 \mu\text{m}$ , revealing that nuclei actually did form even within the first half minute, although they were too small to be visible in Fig. 2(a). In addition, a comparison of the nucleus size and the deposition time (14.5 min in total) with those in Fig. 2(d) ( $0.3 \mu\text{m}$ , 5 min nucleation only) and Fig. 2(e) ( $0.4 \mu\text{m}$ , 5 min nucleation plus 10 min growth) further confirms that the deposition rate under 1 torr was higher than that under 20 torr.

Compare with Group I, we see that the final nucleation density at the substrate temperature  $850^\circ\text{C}$  was lower than that at  $810^\circ\text{C}$ .

The effect of  $\text{CH}_4$  under very low pressure was investigated in experiment Group III. Fig. 3 shows the SEM images of the samples after 2.5 min nucleation with the  $\text{CH}_4$  concentration of (a) 0.35, (b) 0.7 and (c) 6 vol. % while all the other conditions were the same as in Group II, since Fig. 2(c) is also considered as one of this group. The nuclei, if any, are invisible in Fig. 3(a), as the methane concentration was too low. For 0.7 vol. %, several nuclei, can be seen as tiny white spots (smaller than  $0.1 \mu\text{m}$ ) from Fig. 3(b), implying a density of  $\sim 10^6 \text{ cm}^{-2}$ . For high  $\text{CH}_4$  concentration in Fig. 3(a), the density was approximately  $8 \times 10^8 \text{ cm}^{-2}$  with an average nucleus size of  $\sim 0.22 \mu\text{m}$ . While the density in Fig. 2(c), corresponding to  $[\text{CH}_4] = 3 \text{ vol. \%}$ , was much higher than that in Fig. 3(b), the density at 6 vol. % (Fig. 3(c)) was even higher. This demonstrates that a higher  $\text{CH}_4$  concentration led to a higher nucleation rate and a higher density, and that a too low concentration was not suitable for nucleation.

The effect of pressure was further checked in experiment Group IV, as shown in Fig. 4, the SEM image of a sample after 5 min nucleation under pressure 10 torr. The other conditions was the same as in Group II. The nucleation density was approximately  $5 \times 10^7 \text{ cm}^{-2}$  with an average nucleus size of  $\lesssim 0.2 \mu\text{m}$ . This is the typical density obtained under normal pressure (tens of torr), one order of magnitude lower than that under 1 torr with all the other conditions being the same (Fig. 2(d)), not alone that in Fig. 1(a). This also confirms that the high nucleation density in Fig. 2(f) was indeed a result of the nucleation within the first half minute.

#### IV. DISCUSSIONS

Usually, under normal pressure (tens of torr), it takes 30 min or longer to get considerable nucleation on scratched Si or Ti substrates, and the density is no larger than  $10^7$ - $10^8 \text{ cm}^{-2}$ . Compare with our results obtained under a much lower pressure (1 torr) in Fig. 1 and Fig. 2,

it is clear that both the nucleation rate and the nucleation density were dramatically enhanced by the very low pressure, for which the density was 1-3 orders of magnitude higher and the nucleation took place at a much higher rate. While this enhancement was mainly attributable to the much longer mean free path of the gaseous species under the much low pressure,<sup>10</sup> overly higher substrate temperature gave rise to lower nucleation density, and higher CH<sub>4</sub> concentration led to higher rate and density, which revealed more information about the nucleation mechanism.

Generally speaking, various processes take place on/near the substrate surface during nucleation.<sup>18</sup> The carbon ad-atoms may diffuse into the substrate and form carbide; the substrate atoms may also diffuse out of the bulk, and also form carbide. These two processes make nucleation more difficult. It requires a sufficient high amount of carbon and/or hydrocarbon species to achieve a high supersaturation so that nuclei can still form in spite of these two processes. There exists a competition between the formation of carbide and diamond nuclei. In addition, the ad-species may move along the substrate surface, as the substrate temperature is pretty high. The larger the mobility, the more difficult to form stable nuclei. While various phases of carbon may form, it is necessary to select *sp*<sup>3</sup> (diamond) preferentially and suppress the formation of *sp* and *sp*<sup>2</sup> (various forms of non-diamond carbon). This will require a large amount of atomic hydrogen on/near the substrate surface, which also plays a critical role in creating nucleating sites. Therefore, higher concentration and supersaturation of hydrocarbon species on the substrate surface makes it easier for them to accumulate to form nuclei, whereas higher mobility of the ad-species and higher diffusivity of carbon atoms hinder the nucleation process.

For Ti substrate, the diffusion of carbon and Ti atoms is more serious for other substrates such as Si. As can be seen from Fig. 1-4, the TiC layer is very loose and porous, which makes it very easy for the carbon atoms to diffuse into the bulk of the substrate and for the Ti atoms to come out. Actually, carbon atoms have the highest diffusivity in TiC among all carbides, which makes the formation of thick TiC layers extremely easy and thus the nucleation very difficult. Under normal pressure, a long, continuous process of nucleation and formation of TiC is observed, usually.<sup>14</sup> This makes it extremely important to achieve very high supersaturation of carbon on the substrate surface so that a high-density, continuous layer of diamond nuclei forms within a short time and thus the diffusion and the formation of carbide is highly suppressed.

As discussed in detail in ref. 10, the pressure of 1 torr is 1-2 orders of magnitude lower than tens of torr. The mean free path of the gaseous species,  $\lambda$ , which is inversely proportional to the pressure, is thus increased by a factor of several tens. Moreover, the probability for an atom or a molecule to travel a distance  $x$  without collisions,  $e^{-x/\lambda}$ , depends exponentially on  $\lambda$ . Therefore, an

increase of  $\lambda$  by one order of magnitude can increase the probability by many orders of magnitude. The reactive hydrocarbon radicals are mainly generated in the neighborhood of the hot filament while the deposition takes place on the substrate at a distance ( $x = 8$  mm in our experiments). The mean free path can be estimated using the formula  $\lambda = k_B T / (\sqrt{2} \pi \bar{d}^2 p)$ , where  $\bar{d}$  is the sum of the radii of the two colliding atoms/molecules,  $k_B$  is the Boltzman constant,  $T$  is the temperature and  $p$  is the pressure. We take  $T \sim 1700^\circ\text{C}$  as an average temperature between the filament and the substrate. As the gas is composed mainly of molecular hydrogen, we take the radii of H atoms, H<sub>2</sub> molecules and CH<sub>x</sub> species to be approximately 0.75 Å, 1.0 Å and 1.6 Å, respectively.<sup>19</sup> Thus, the mean free path for hydrogen atoms is estimated to be 0.13 mm and 1.3 mm under 10 torr and 1 torr, respectively. For hydrocarbon species, it is approximately 0.06 mm and 0.6 mm under 10 torr and 1 torr, respectively. Then the probability for an H atom created by the filament to transport to the substrate will increase from  $\sim 10^{-27}$  to  $\sim 10^{-3}$  when the pressure changes from 10 torr to 1 torr, and that for a hydrocarbon radical will increase from  $\sim 10^{-58}$  to  $\sim 10^{-6}$ ! As the radii of the gas species can not be exact, these exponentials may vary quite a lot depending on the values of the radii used. Nonetheless, the big difference remains within a reasonable range of the radii. Therefore, the concentration of both the reactive hydrocarbon radicals and atomic hydrogen is dramatically increased on/near the substrate surface, so is the supersaturation of carbon. The increase amount of atomic hydrogen is critical to generate a large density of nucleating sites and guarantee that diamond is formed, not just non-diamond carbon. This is the main reason why the nucleation is greatly enhanced under very low pressure.

Apart from the long mean free path, other effects of the very low pressure also contribute. Under very low pressure in our experiments, there existed a strong current of electrons emitted from the hot filament, which was 0.5 A or higher. The energy of the electrons ranged from 0 up to  $\sim 80$  eV, high enough to decompose the hydrocarbon species in a collision. As we found earlier, the energetic electrons could result in an increase of the concentration and the kinetic energy of atomic hydrogen and reactive hydrocarbon radicals.<sup>9,7</sup> Due to the long mean free path, more energetic, reactive hydrocarbon radicals arrive at the substrate since the filament temperature is much higher than that of the environment. In addition, under lower pressure, the filament can decompose the gas more effectively.<sup>20,21</sup> These effects also add to the supersaturation of the reactive hydrocarbon species on the substrate surface, presenting a nucleation enhancement effect.

Comparison of the nucleation density between Fig. 1 and Fig. 2 reveals that higher substrate temperature leads to a lower nucleation density. The diffusivity of a carbon atom into the substrate or of a Ti atom out of

the substrate is proportional to  $e^{-(W_d - E)/k_B T}$ , where  $E$  is the energy of the atom,  $W_d$  is the corresponding energy barrier against diffusion, and  $T$  is the substrate temperature,  $\sim 800^\circ\text{C}$ . Suppose  $W_d$  is independent of temperature, then at higher substrate temperature,  $E$  is higher and  $k_B T$  is larger, therefore, the diffusivity is larger. This then requires a higher supersaturation of carbon to nucleate. Also higher temperature leads to a much higher surface mobility of the ad-species, which is similarly proportional to  $e^{(E-W_m)/k_B T}$ . Now  $W_m$  is the energy barrier against the movement on the surface. Presumably, it is very small, even smaller than the kinetic energy of the ad-species. Therefore, at higher temperature, a larger part of the carbon is used to form carbide, and also it is much more difficult for the hydrocarbon ad-species to conglomerate at some nucleating sites to form stable diamond nuclei. In result, a lower nucleation density is observed at a lower rate, as shown in Fig. 2.

The  $\text{CH}_4$  concentration is naively also an important factor. Obviously, the concentration of the hydrocarbon species near/on the sample surface is proportional to it. Fig. 3(a), (b), Fig. 2(c), and Fig. 3(c) show a continuous increase of the nucleation rate and the nucleation density. A too low concentration, e.g., 0.35 vol. % in Fig. 3(a), is insufficient to form nuclei as the diffusivity of carbon into the Ti substrate is too high, and all the hydrocarbon radicals are actually converted into  $\text{TiC}$ . Higher  $\text{CH}_4$  concentration builds up a higher supersaturation of hydrocarbon on the substrate surface, and thus enhances nucleation.

Our estimate about the mean free path seems to indicate that the pressure effect dominate, making all other factors unimportant. However, a comparison of Fig. 3 and Fig. 4 tells that it is not the case. Fig. 3 shows a strong influence of the  $\text{CH}_4$  concentration. A too low  $\text{CH}_4$  concentration could not lead to high density nucleation, although the pressure was very low (1 torr, Fig. 3(a)). On the other hand, at normal pressure (10 torr, Fig. 4), high  $\text{CH}_4$  concentration could also lead to considerable nucleation, though the density is not high. This sheds some light on the mechanism of nucleation.

First, not all collisions result in loss of reactive hydrocarbon radicals and/or atomic hydrogen through recombination, as the gas is mainly composed of molecular hydrogen. The  $\text{CH}_4$  concentration is typically less than 5 vol. %. In addition, only a small percentage of  $\text{CH}_4$  is decomposed to  $\text{CH}_x$  ( $x < 4$ ). The total amount of atomic hydrogen is estimated to be of the order of 1%. Therefore, the chance for an H atom or a  $\text{CH}_x$  radical to meet an H atom or  $\text{CH}_x$  is reduced by a factor of  $\sim 100$ . In addition, even collisions between, say, two H atoms does not necessarily lead to recombination. Thus, the effective “mean free path” in terms of recombination may be over ten times larger, if we do not consider the energy exchange in collisions. In result, the effect of very low pressure may not be as strong as estimated earlier. Even so, the probability for an H atom and a  $\text{CH}_x$  radical to get onto the substrate without recombination is still en-

hanced by a factor of  $\sim 10^2$  and  $\sim 10^5$ , respectively when the pressure is lowered from 10 torr to 1 torr.

Second, some hydrocarbon radicals, such as  $\text{C}_2\text{H}_x$  ( $x < 6$ ), which also contribute to nucleation and growth,<sup>18,22–24</sup> are actually created through collisions between  $\text{CH}_x$  ( $x \leq 4$ ).<sup>24</sup> Their concentration may decrease when pressure is lowered. In addition, some collisions may result in exchange between an H atom and a methyl radical, such as  $\text{H} + \text{CH}_4 \rightleftharpoons \text{H}_2 + \text{CH}_3$ , which is not necessarily unfavorable for nucleation.

Third, apart from  $\text{CH}_{1-3}$ ,  $\text{CH}_4$  also contributes to the nucleation and growth process as it can be converted into methyl radical in the vicinity of the substrate.<sup>18,22</sup> Its concentration of  $\text{CH}_4$  is basically independent of its mean free path. Carat and Goodwin studied the change of  $\text{CH}_3$  concentration near the substrate surface with the substrate temperature under normal pressure, and showed an considerable increase when the substrate temperature increased from  $700^\circ\text{C}$  to  $1000^\circ\text{C}$ , while the concentration of  $\text{C}_2\text{H}_x$  remained unchanged.<sup>25</sup> Four millimeters away from the substrate, the  $\text{CH}_3$  concentration was much less dependent on the substrate temperature. At  $\sim 660^\circ\text{C}$ , the concentration of  $\text{CH}_3$  near the substrate surface was very small, only about 20% of that at 4 mm away. At this substrate temperature, the contribution of the substrate is small, and the  $\text{CH}_3$  was mainly from decomposition of  $\text{CH}_4$  by the filament. At  $800^\circ\text{C}$ , the ration increased to 40%. This shows that considerable part of  $\text{CH}_3$  is actually generated from  $\text{CH}_4$  on/near the substrate under normal pressure. This factor makes the total  $\text{CH}_3$  concentration deviate from the exponential falloff versus distance from the filament, especially in the neighborhood of the substrate surface, so that a considerable, though poor, nucleation density is still observed under normal pressure. However, the substrate temperature is too low to decompose  $\text{CH}_4$  effectively. Nonetheless, the contribution of  $\text{C}_2\text{H}_x$  and  $\text{CH}_4$  (through  $\text{CH}_3$ ) has to be assumed to explain the nucleation behavior under normal pressure.

Last, the hydrocarbon precursors for deposition are mainly  $\text{CH}_{1-3}$  and  $\text{C}_2\text{H}_x$ . The former is from the decomposition of  $\text{CH}_4$  partly by filament and partly by the substrate. The latter is mainly from chemical reaction between methyl radicals during transportation from the filament to the substrate. Both have comparable contribution to the nucleation under normal pressure. Using the result of Carat and Goodwin,<sup>25</sup> the  $\text{CH}_3$  concentration due to the filament falls off by a factor of at least 25 for a distance of 8 mm (the substrate-filament distance in our experiments). Under very low pressure, the mean free path is much longer, and thus, the part of  $\text{CH}_{1-3}$  due to the filament is dramatically increased, while the other part and the  $\text{C}_2\text{H}_x$  concentration do not increase. The strong effect of the pressure reveals that  $\text{CH}_4$  and  $\text{C}_2\text{H}_x$  do not contribute much under very low pressure, as compared with  $\text{CH}_{1-3}$ . Frenklach suggested that the H-abstraction- $\text{C}_2\text{H}_2$ -addition mechanism dominates among various deposition reactions.<sup>24</sup> However,

this does not seem to be true in our case, as lowering pressure actually somehow decrease the concentration of  $C_2H_x$ . In agreement with our argumentation, Wu and Hong's recent work also suggests that  $CH_3$  is the main hydrocarbon precursor for diamond deposition, whereas  $C_2H_2$  is not efficient in diamond deposition.<sup>28</sup>

On the other hand, if we assume that the effect of a pressure change from 10 torr to 1 torr was approximately countered by the change of  $CH_4$  concentration from 3 vol. % to 0.3 vol. %, then the effective mean free path of  $CH_x$  in terms of recombination would be about 50 times that in terms of collision. If this was true, then the probability for, say, a  $CH_3$  radical and an H atom to recombine when colliding would be smaller than 10%. However, due to the inaccuracy of the radii of various gas species and to the contribution of  $CH_4$  and  $C_2H_x$ , the actual situation is much more complicated.

It is worth mentioning that the nucleation seems to take place preferentially on protruding convex features of the surface, as can be seen from the SEM images. As suggested by Dennig and Stevenson, this may be attributed to a minimized interfacial energy and more dangling bonds, etc at these sites. However, the model of enhanced nucleation at sites with concave curvature on a 2-dimensional surface by Louchev *et al* is yet to be verified.<sup>27</sup>

In spite of all the difficulties in getting accurate information, it is clear that a very low pressure increases the mean free path, greatly increases the concentration of reactive hydrocarbon radicals and atomic hydrogen, and builds up supersaturation of hydrocarbon on the substrate surface, which is necessary for nucleation. The obvious effect of the  $CH_4$  concentration indicates that  $C_2H_x$  and even  $CH_4$  also contribute to the deposition process, though far less than  $CH_{1-3}$  does under very low pressure.

Since this method can achieve high density nucleation at a very rapid rate, it can greatly reduce the duration for nucleation and thus solve to a large extent the serious problems of hydrogenation and the formation of thick carbide layers, as reported in ref. 17. Further work is necessary to optimize the experimental parameter to minimize hydrogenation and the formation of carbide.

The pressure effect can be used to promote the growth rate of diamond. As  $CH_{1-3}$  is one of the main hydrocarbon precursors, a relatively lower pressure should be used to increase the mean free path, and the filament-substrate distance should be as short as possible, since the probability for a methyl radical to move without collisions from the filament to the substrate depends exponentially on both the pressure and the distance. In this situation, the surface morphology of the resulting films may be different from that under normal pressure, as the ratio of concentration between  $CH_{1-3}$  and  $C_2H_x$  is changed for the above reasons; this ration determines which facet, (111) or (100), of diamond to appear finally.<sup>23</sup>

## V. SUMMARY

Very rapid nucleation was obtained on titanium substrates with a high density ranging from  $10^8 \text{ cm}^{-2}$  to  $10^{10} \text{ cm}^{-2}$ , 1-3 orders of magnitude higher than that obtained under normally low pressure of tens of torr. The nucleation process was studied in detail, revealing that rapid, high-density nucleation could occur within the first half minute. The effects of temperature and  $CH_4$  effects indicates that, in addition to  $CH_{1-3}$ ,  $C_2H_x$  and  $CH_4$  also contribute in nucleation. On the other hand, the strong pressure effect indicates that their role is much less important than that of  $CH_{1-3}$  under very low pressure. All these can be explained in terms of the supersaturation of carbon and/or hydrocarbon species on/near the substrate surface, which is a prerequisite for nucleation. There exists a competition between the diffusion of carbon atoms to form carbide and the nucleation process. As the formation of TiC is so easy for titanium substrate, relatively lower substrate temperature should be used to reduce the diffusivity of carbon atom and to decrease the rate of the formation of TiC. Furthermore, high supersaturation of carbon is necessary to satisfy both processes at the very beginning so that a layer of high density nuclei is formed quickly to suppress the formation of TiC. With a considerably high  $CH_4$  concentration, very low pressure leads to an increased mean free path, exponentially increases the concentration of atomic hydrogen and reactive hydrocarbon radicals, especially,  $CH_{1-3}$ , near/on the substrate surface. While atomic hydrogen is critical in generating a high density of nucleating sites and guaranteeing the formation of diamond, high hydrocarbon concentration helps to win the competition against the quick formation of carbide. This method has solved the problems of hydrogenation and carbide formation to a very large extent. It also implies that lower pressure and shorter filament-substrate distance may result in greatly enhanced growth rate.

<sup>1</sup> *The properties of Diamond*, edited by J. E. Field, (Academic, London, 1979)

<sup>2</sup> D. G. Jeng, H. S. Tuan, R. F. Salat and G. J. Fricano, *Appl. Phys. Lett.* **56**, 1968(1990)

<sup>3</sup> S. Yugo, T. Kanai, T. Kimura and T. Muto, *Appl. Phys. Lett.* **58**, 1036(1991)

<sup>4</sup> B. R. Stoner, G.-H. M. Ma, S. D. Wolter and J. T. Glass, *Phys. Rev. B* **45**, 11067(1992)

<sup>5</sup> S. D. Wolter, T. H. Borst, A. Vescan and E. Kohn, *Appl. Phys. Lett.* **68**, 3558(1996)

<sup>6</sup> W. Zhu, F. R. Sivazlian, B. R. Stoner and J. T. Glass, *J. Mater. Res.* **10**, 425(1995)

<sup>7</sup> Q. Chen and Z. Lin, *Appl. Phys. Lett.* **68**, 2450(1996)

<sup>8</sup> Q. Chen and Z. Lin, *J. Appl. Phys.* **80**, 797(1996)

- <sup>9</sup> Q. Chen, Y. Chen, J. Yang and Z. Lin, Thin Solid Films **274**, 160(1996)
- <sup>10</sup> Q. Chen, *Investigation of Diamond Nucleation under Very Low Pressure in Chemical Vapor Deposition*, preprint cond-mat/9708146
- <sup>11</sup> X. Jiang, K. Schiffmann and C.-P. Klages, Phys. Rev. **B50**, 8402(1994)
- <sup>12</sup> D. S. Shih, I. M. Robertson and H. K. Birnbaum, Acta Metall. **36**, 111(1988)
- <sup>13</sup> H. Numakura and M. Koiwa, Acta Metall. **32**, 1799(1984)
- <sup>14</sup> S.-S. Park and J.-Y. Lee, J. Appl. Phys. **69**, 2618(1991)
- <sup>15</sup> B. R. Stoner and J. T. Glass, Appl. Phys. Lett. **60**, 698(1992); S. D. Wolter et al, Appl. Phys. Lett. **62**, 1215(1993); W. Zhu et al, Phys. Rev. **B47**, 6529(1993)
- <sup>16</sup> B. R. Stoner et al, Diamond Relat. Mater. **2**, 142(1993)
- <sup>17</sup> Q. Chen and Z. Lin, J. Mater. Res. **10**, 2685(1995)
- <sup>18</sup> J. C. Angus, Y. Wang and M. Sunkara, Annu. Rev. Mater. Sci. **21**, 221(1991); J. C. Angus and C. C. Hayman, Science **241**, 913(1988)
- <sup>19</sup> The radii of hydrogen and carbon atoms differ from different sources. Also they also depend on how they are determined. We take the average of their covalent radii and their Van der Waals radii for estimation purpose. The radii of H<sub>2</sub> molecules and CH<sub>x</sub> are estimated based on those of H atoms and C atoms.
- <sup>20</sup> N. Setaka, J. Mater. Res. **4**, 664(1989)
- <sup>21</sup> M. Katoh, M. Aoki and H. Kawarada, Jpn. J. Appl. Phys. **33**, L194(1994)
- <sup>22</sup> B. Sun, X. Zhang and Z. Lin, Phys. Rev. **B47**, 9816(1993)
- <sup>23</sup> K. E. Spear, J. Am. Ceram. Soc. **72**, 171(1989)
- <sup>24</sup> M. Frenklach and H. Wang, Phys. Rev. **B43**, 1520(1991)
- <sup>25</sup> E. J. Carat and D. G. Goodwin, J. Appl. Phys. **74**, 2021(1993)
- <sup>26</sup> P. A. Dennig and D. A. Stevenson, Appl. Phys. Lett. **59**, 1562(1991)
- <sup>27</sup> O. A. Louchev, Y. Sato and P. A. Dennig, Appl. Phys. Lett. **71**, 894(1997)
- <sup>28</sup> J.-J. Wu and F. C.-N. Hong, Appl. Phys. Lett. **70**, 185(1997)

FIG. 1. SEM images of samples in Group I after (a) 2 min, (b) 3 min nucleation under 1 torr and (c) 3 min nucleation under  $p = 1$  torr plus 10 min growth under  $p = 20$  torr. (d) is the same as (a) but with a lower magnification.  $T_s = 810^\circ\text{C}$  for nucleation. Nucleation did not occur preferentially along the scratch marks. The density was as high as  $10^{10} \text{ cm}^{-2}$ .

FIG. 2. SEM images of samples in Group II after (a) 0.5 min, (b) 1 min, (c) 2.5 min, (d) 5 min nucleation, (e) 5 min nucleation plus 10 min growth and (f) 0.5 min nucleation plus 14 min growth. The pressure for nucleation and growth was 1 torr and 20 torr, respectively.  $T_s = 850^\circ\text{C}$  for nucleation. Nucleation reached its final density,  $\sim 4 \times 10^8 \text{ cm}^{-2}$ , within 2.5 min, and (f) shows that nucleation occurred during the first half minute. The density was lower than that in Group I.

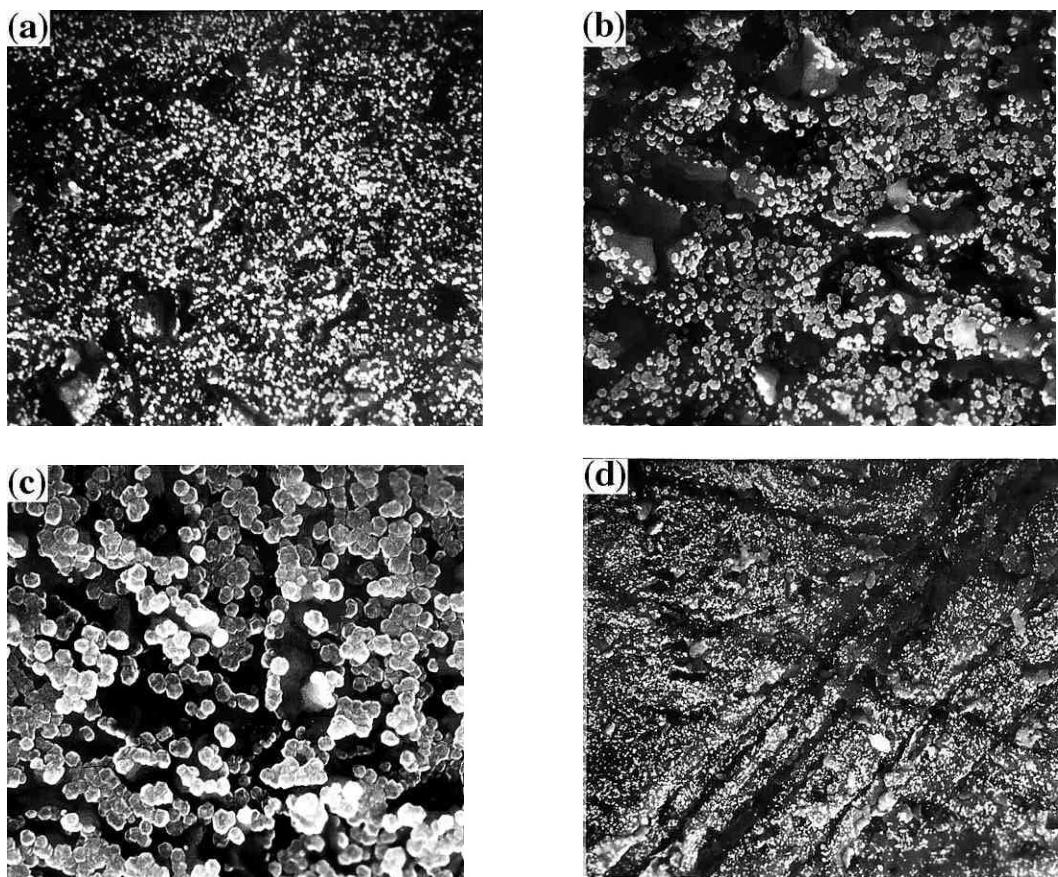
FIG. 3. SEM photos of samples in Group III after 2.5 min nucleation under  $p = 1$  torr and different CH<sub>4</sub> concentrations: (a) 0.35, (b) 0.7 and (c) 6 vol. %. Also consider Fig. 2(C) as one of this group. The density increased with increasing CH<sub>4</sub> concentration.

FIG. 4. SEM image of a sample after 5 min nucleation under 10 torr. The density,  $\sim 5 \times 10^7 \text{ cm}^{-2}$ , was one order of magnitude lower than that obtained under 1 torr while all other conditions were the same (Fig. 3(d)).

TABLE I. Experimental parameters for nucleation.

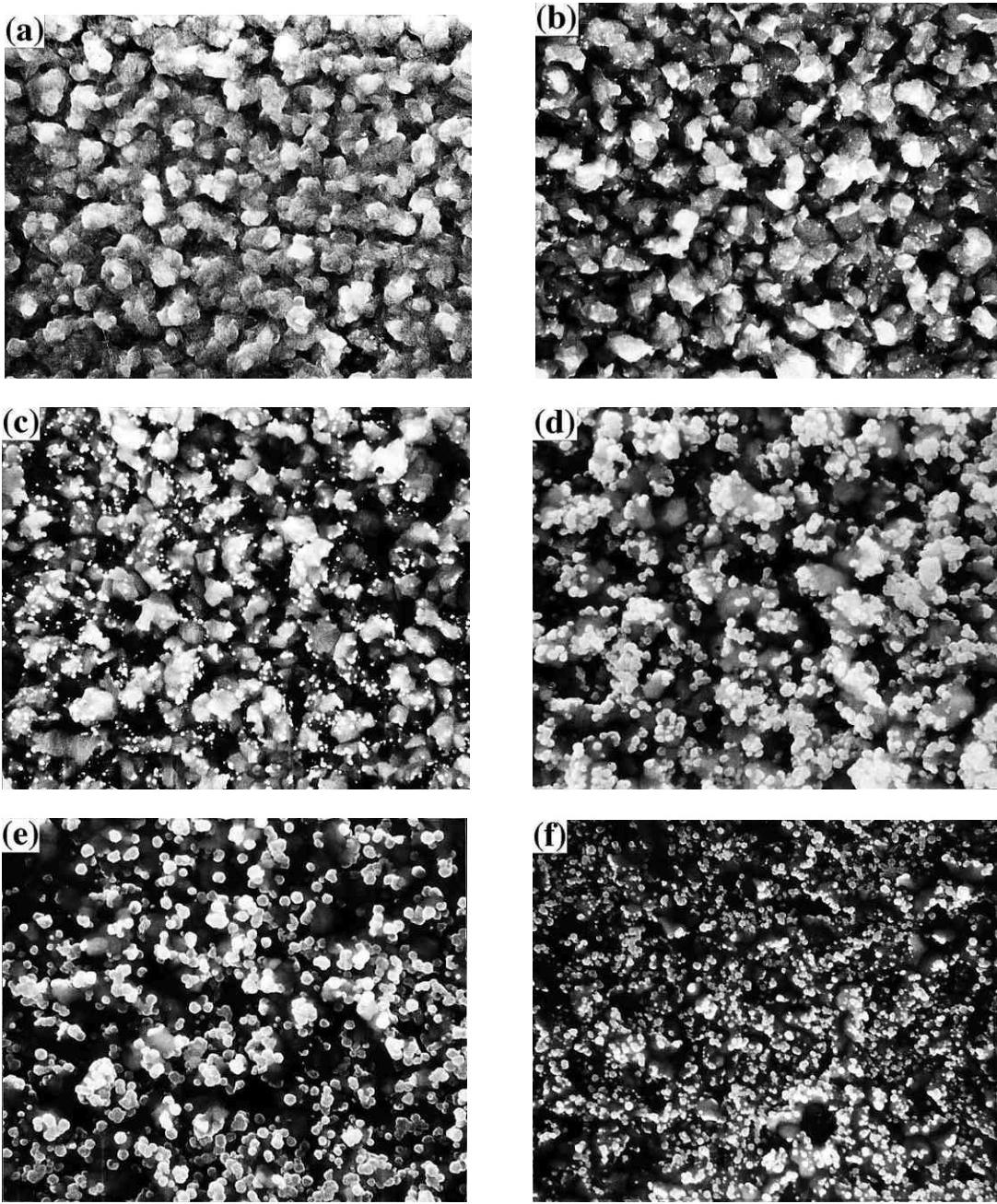
parameters	Notations	Group I	Group II	Group III	Group IV
Flow rate (sccm) <sup>a</sup>	$F$	77	72	70	72
CH <sub>4</sub> concentr. (vol.%)	[CH <sub>4</sub> ]	3.0	3.0	0.35-6.0	3.0
Filament temp. (°C)	$T_f$	2050	2050	2050	2050
Substrate temp. (°C)	$T_s$	810	850	850	850
pressure (torr)	$p$	1	1	1	10
duration (min)	$t$	2, 3	0.5-5.0	2.5	5

<sup>a</sup>sccm denote cubic centimeter per minute at STP.



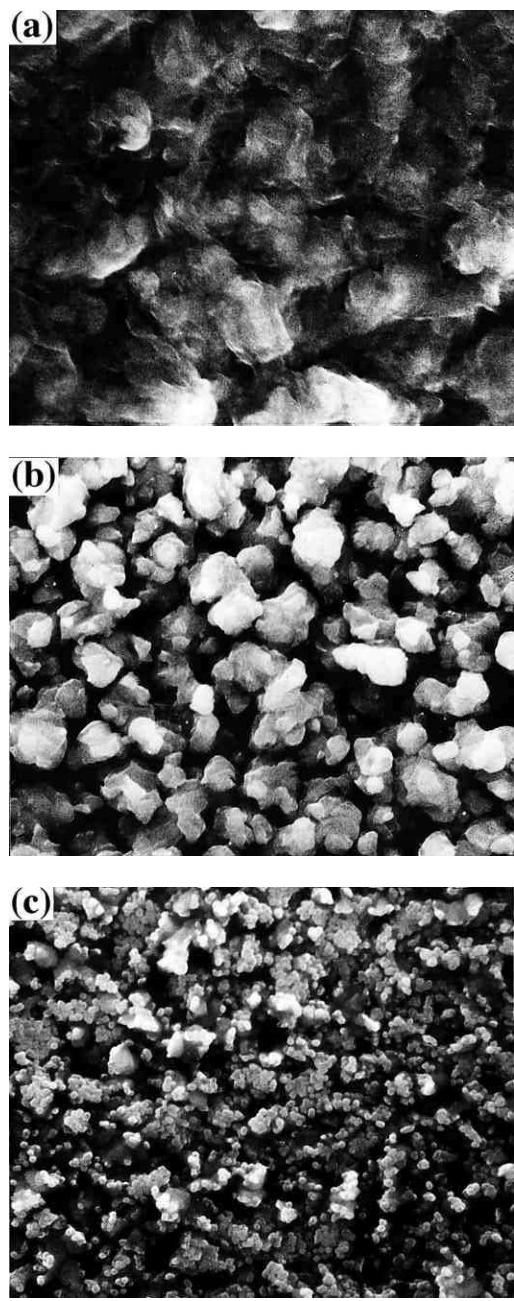
$\overline{1.5 \mu\text{m}}$

Figure 1



3  $\mu$ m

Figure 2



3  $\mu$ m

Figure 3

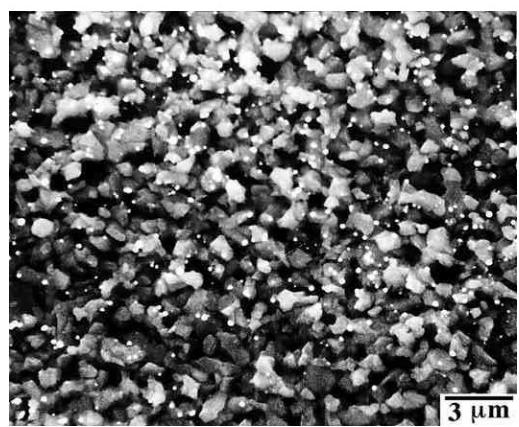


Figure 4